ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF ENFORCEMENT

REPORT ON
EVALUATION OF INDUSTRIAL WASTE DISCHARGES
AT
CITIES SERVICE OIL COMPANY
LAKE CHARLES OPERATIONS
LAKE CHARLES, LOUISIANA

Prepared By

DIVISION OF FIELD INVESTIGATIONS - DENVER CENTER
DENVER, COLORADO

AND

REGION VI DALLAS, TEXAS

CLEAN WATER

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INTRODUCTION

Louisiana's second largest industrialized area is located near Lake Charles in the Calcasieu River Basin in the southwestern corner of the State. Industries in the Lower Calcasieu area are primarily involved in the production of chemical, petrochemical, and petroleum products.

These industries discharge waste waters into the Calcaseiu River or its tributaries - Bayou d'Inde, Bayou Verdine, Houston River, Mill Creek, and Palmetto Creek. The Rivers and Harbors Act of 1899,[1/] the Water Quality Act of 1965, and the Water Quality Improvement Act of 1970[2/] are applicable to the Calcasieu River and its tributaries. [Water quality regulations established pursuant to the provisions of these Acts are presented in Appendix A.]

The Division of Field Investigations-Denver Center (DFI-DC), Environmental Protection Agency (EPA), at the request of the Director, Water Quality Office, Region VI, EPA, undertook a study of the Calcasieu River Basin in March-April 1971. Specific objectives of the study were to:

1. Compile an up-to-date inventory of industrial waste sources discharging to the Calcasieu River and its tributaries.
2. Ascertain a) types of treatment presently provided and b) the quality and quantity of each industrial waste discharge.
3. Evaluate the individual and collective impacts of wastewater discharges on the beneficial water uses of the Calcasieu River and its tributaries.
4. Determine abatement proceedings necessary or warranted under the Rivers and Harbors Act of 1899, the Water Quality Act of

1965, and/or other applicable local, State and Federal laws.

This report summarizes information pertaining to raw materials, processes, waste loads, and treatment needs at the various plants of the Cities Service Oil Company, Lake Charles, Louisiana, and recommends actions necessary to protect the quality of the receiving waters. Complete custodial records [Appendix B], for each sample taken during the course of this investigation, are on file in the Denver, Colorado, office of the Division of Field Investigations-Denver Center.

Assistance and support in the conduct of this investigation was provided by the following EPA entities:

Division of Field Investigations-Cincinnati Center

Analytical Quality Control Laboratory, Cincinnati, Ohio

Enforcement Office, Region VI, Dallas, Texas

Southeast Water Laboratory, Athens, Georgia

The assistance of personnel of the Lake Charles Office, Louisiana Wildlife and Fisheries Commission, is gratefully acknowledged.

BACKGROUND INFORMATION

General

The total drainage area of the Calcasieu River and its tributaries equals about 4,000 square miles; measures approximately 120 miles in length and 55 miles in width; and includes portions of eight different parishes (population - about 230,000). [See Figure 1.] The Lower Calcasieu River encompasses the area downstream from a salt water barrier (located just north of the city of Lake Charles) to the Gulf of Mexico. The Upper

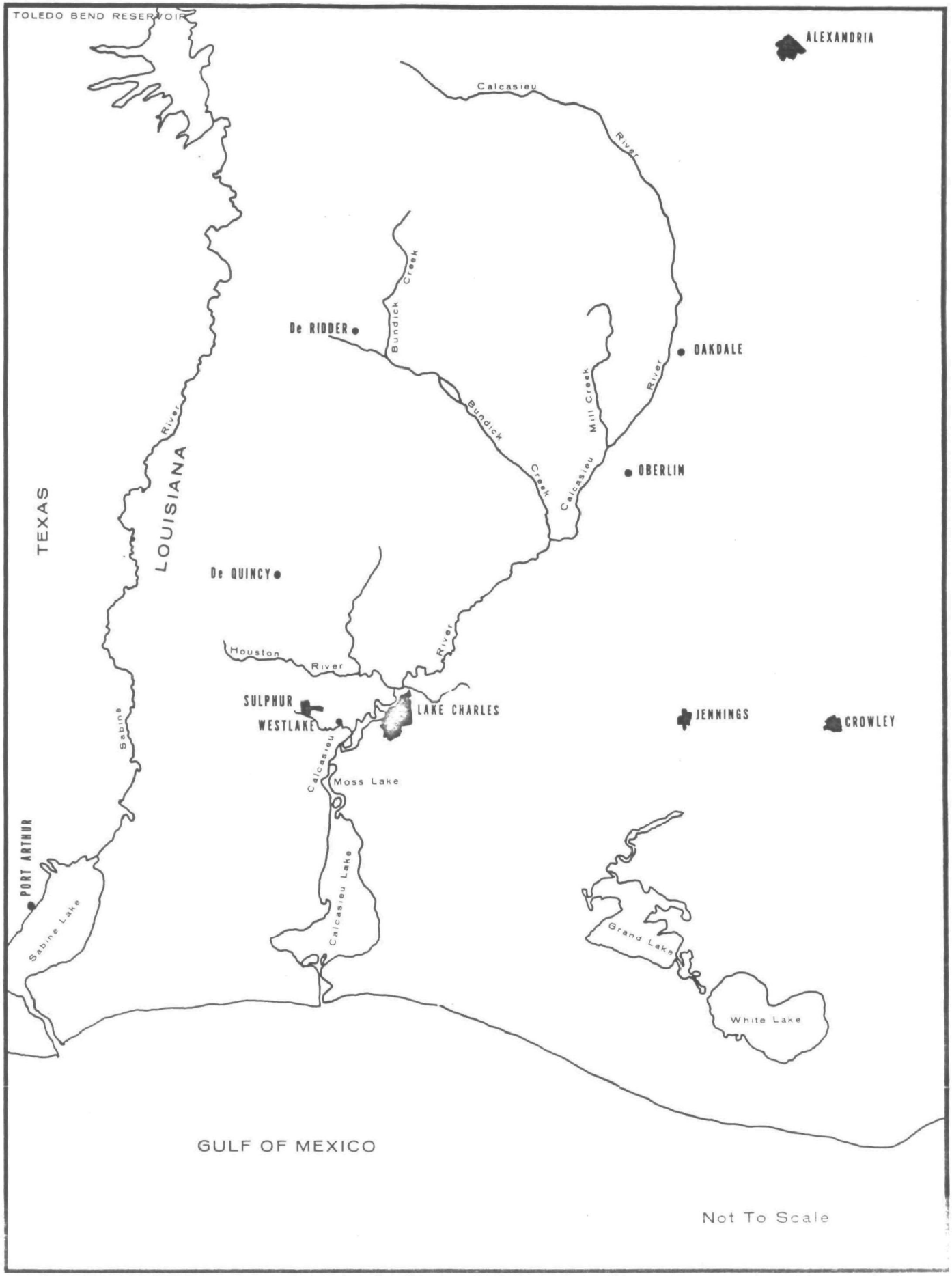

Figure 1. Location Map - Calcasieu River Drainage

Calcasieu River consists of the fresh water portion of the watershed extending upstream from the salt water barrier to the basin headwaters.

The River is navigable upstream to Moss Bluff, Louisiana (about ten miles upstream from Westlake).[3/] Barges and ships navigate a channel that has been dredged from the Gulf of Mexico northward along the west side of Calcasieu Lake to Devils Elbow, thereafter following the natural river channel, except for two cutoffs, to the Port of Lake Charles.

Thundersqualls and tropical storms with high wind velocities occasionally pass through the area. Prevailing winds are primarily from the north during months of November through January and from the south during the remainder of the year. Frosts are experienced from late November to late February. Average temperatures range from the low 50's (in January) to the 80's (in July).

The Lower Calcasieu River, Lake Calcasieu, Bayou d'Inde, Bayou Verdine, and Indian Marais are affected by lunar tides. Passage of a cold front or high winds may cause wind-dominated tides that produce flooding of low-lying areas and tributary streams and bayous. As a result of these events, flow and mixing patterns may be highly irregular.

Brackish inland lakes and marshes that border the main River channel and the adjacent shallow offshore area support a large commercial and sport fishery. The area is an excellent spawning and rearing ground for shrimp, crabs, and various estuarine fish.

In addition to furnishing a location for the propagation of aquatic life, the waters of the Calcasieu River system and its tributary streams support other beneficial activities, including municipal and industrial

water supplies, recreation, irrigation, and navigation.

In conjunction with other chemical plants and petroleum refineries, the Cities Services Oil Company plants are substantial contributors to the economy in the Lower Calcasieu River area. Company operations are involved in the production of petroleum products, petrochemicals, and butyl rubber.

Chronology of Contacts

The Cities Service Oil Company (P. O. Box 1562, Lake Charles, Louisiana 70601) has four industrial plants located in the Lake Charles area:

(1) Cities Service Oil Company Butyl Rubber;

(2) Cities Service Oil Company Refinery;

(3) Cities Service Oil Company Lube and Wax; and

(4) Cities Service Oil Company Petrochemical and Ethylene Propylene.

On March 25, 1971, W. C. Blackman, Jr., M. R. Helton, and J. L. Hatheway, DFI-DC, EPA, met with T. W. Kirby, assistant superintendent for laboratories, at the Cities Service Oil Company, in order to obtain information for a waste source inventory. T. P. Harrison, Enforcement Office, EPA, Region VI, had made arrangements for the meeting. A tour of the four plants was conducted during the March 25 visit. (Mr. Kirby would not permit the investigators to take photographs within the plant property).

Subsequent contact was made with Mr. Kirby on April 15, by R. D. Harp and Mr. Hatheway, both of DFI-DC, to plan the industrial waste sampling program being conducted in conjunction with a water quality survey of the Calcasieu River Basin. Mr. Kirby was informed that the survey information would be used as the basis for:

(1) Evaluation of Corps of Engineers permits as required under the

Rivers and Harbors Act of 1899;

(2) Determination of present water quality conditions in the Calcasieu River and its tributaries;

(3) Evaluation of the individual and collective impacts of wastewater discharges on the beneficial water uses of the Calcasieu River and its tributaries;

(4) Determination of water pollution control needs within the area;

(5) Abatement proceedings as necessary or warranted under the Rivers and Harbors Act of 1899, the Water Quality Act of 1965, and/or other applicable local, State and Federal laws.

Permission to sample all effluent discharges was granted; however, permission to sample process wastes prior to treatment was not granted.

Pertinent information and results of the investigation of waste treatment and disposal practices at each Cities Service facility are discussed below.

BACKGROUND INFORMATION

Facility Description

The Butyl rubber plant operates continuously. Eighty-seven people are employed in the rubber production operation. The rated plant capacity is 84 million lbs per year of Butyl rubber, the plant's primary product. By-products, such as isobutylene, isoprene, and methyl chloride, are recycled into the production process. The raw materials that are employed include isobutylene, isoprene, zinc stearate, aluminum chloride, and natural gas.

Water Supply

Water, for process and cooling purposes, is obtained from one 1,000 gpm (1.44 mgd) well. Boiler feed water is supplied from steam condensate in the refinery feed.

Existing Waste Treatment

Oily wastewaters from the Butyl plant are discharged to the oxidation pond at the Cities Service Oil Company refinery. Once-through cooling water, other wastewater, and blowdown from a cooling tower are discharged to the Lower Calcasieu River without treatment.

The effluent, from a commercial chromate recovery process, is -- according to Company information -- essentially free of chromate, although it may contain zinc on the order of 2-3 mg/l as zinc stearate.

SAMPLING PROGRAM AND RESULTS

Aliquots (125 ml) of the effluent were composited every two hours for 24 hours, commencing at 7:35 a.m., April 21, 1971. Samples were taken from the outfall ditch near the Lower Calcasieu River [Figure 2]. A grab sample was collected, at 3:40 p.m., April 17, for oil and grease analysis. Shrimp survival studies were conducted in the Lower Calcasieu River in the vicinity of this discharge. Water and sediment samples were collected in the Lower River upstream and downstream from the point of industrial discharge. [The sampling points are described in Table 1, their locations shown in Figure 2.]

[Analyses of the effluent and stream samples are listed in Table 2.] During the 24-hour sampling period, pollutant loads discharged included 6 lbs of chromium; 2,470 lbs, chemical oxygen demand (COD); 410 lbs, total organic carbon (TOC); 2,160 lbs, suspended solids; and 100 lbs of oil and grease.

Survival studies using white shrimp were conducted (following methods outlined in Appendix C) in situ at industrial site stations CR-2.1 and 4.2 and at the Control Stations (Cr-11.2 and 1) [Figure 2]. Total mortality, within 24 hours, of the shrimp at CR-4.1 and 4.2, precluded taste and odor studies. After a similar 24-hour exposure period, shrimp mortalities at the Control Stations were 10 and 20 percent, respectively [Table 3]. Although it is not known which constituents or combinations of constituents in the River caused total mortality at stations CR-4.1 and CR-4, it is clear that the stream quality at this location is toxic to native shrimp. [See Table 3.]

TABLE 1

DESCRIPTION OF EFFLUENT AND RECEIVING WATER SAMPLING POINTS

Station Number	Description and Remarks
CSC-1	Samples collected from the drainage ditch at a point just before it empties into the Lower Calcasieu River (ditch parallels the north fence of the Cities Service refinery plant).
CR-1	Lower Calcasieu River near Calcasieu Landing (upstream of intracoastal waterway) near Channel Marker 92 (Control Station).
CR-4	Lower Calcasieu River upstream of Cities Service refinery effluent and downstream from the Butyl rubber plant effluent.
CR-4.1	Lower Calcasieu River, northwest shore, at discharge of the Butyl rubber plant.
CR-4.2	Lower Calcasieu River, opposite the Butyl rubber plant.
CR-5	Lower Calcasieu River near Channel Marker 108.
CR-11.2	Lower Calcasieu River, south shore, south of Clooney Island just west of Lake Charles (Control Station).

TABLE 2

SUMMARY OF ANALYTICAL RESULTS AND FIELD MEASUREMENTS[a/]

Sta	Flow mgd	pH range	Conductivity µmhos/cm range	Conductivity µmhos/cm comp	Temp °C range	TOC mg/l	TOC lbs/day	COD[b/] mg/l	COD[b/] lbs/day	Solids total mg/l	Solids total lbs/day	Solids susp mg/l	Solids susp lbs/day	Oil & Grease mg/l	Oil & Grease lbs/day
CSC-1	1.70	7.2-9.8	1,000-3,500	2,300	22-30.5	29	410	170	2,470	1,480	21,000	152	2,160	7	100
CR-4		7.1-8.3		13,000	24-24	9.4, 12[c/]				8,610		14			
CR-5		6.8-8.6		13,400	23-24	9.4, 13[c/]				8,980		16			

Sta	Cadmium mg/l	Chromium mg/l	Chromium lbs/day	Mercury µg/l	Copper mg/l	Lead mg/l
CSC-1	<0.05	0.40	6	<0.1	<0.02	<0.1
CR-4						
CR-5						

a/ Analytical procedures are outlined in Appendix D.
b/ COD analyses were performed when TOC values exceeded 20 mg/l.
c/ Two composites taken (morning and afternoon).

TABLE 3

PALATABILITY AND IN SITU STUDIES OF WHITE SHRIMP IN THE LOWER CALCASIEU RIVER, LOUISIANA

Station	96-Hour Shrimp Survival Study[a/] Exposure Time	Number Alive	Number Dead	Percent Survival
CR-11.2 (Control)	Initial	10	0	100
	24-hour	9	1	90
	48-hour	8	2	80
	72-hour	8	2	80
	96-hour	5	5	50
CR-5	Initial	10	0	100
	24-hour	6	4	60
	48-hour	4	6	40
	72-hour	3	7	30
	96-hour	1	9	10
CR-4.2	Initial	10	0	100
	24-hour	0	10	0
CR-4.1	Initial	10	0	100
	24-hour	0	10	0
CR-1 (Control)	Initial	10	0	100
	24-hour	8	2	80
	48-hour	8	2	80
	72-hour	8	2	80
	96-hour	5	5	50

a/ April 20-24, 1971

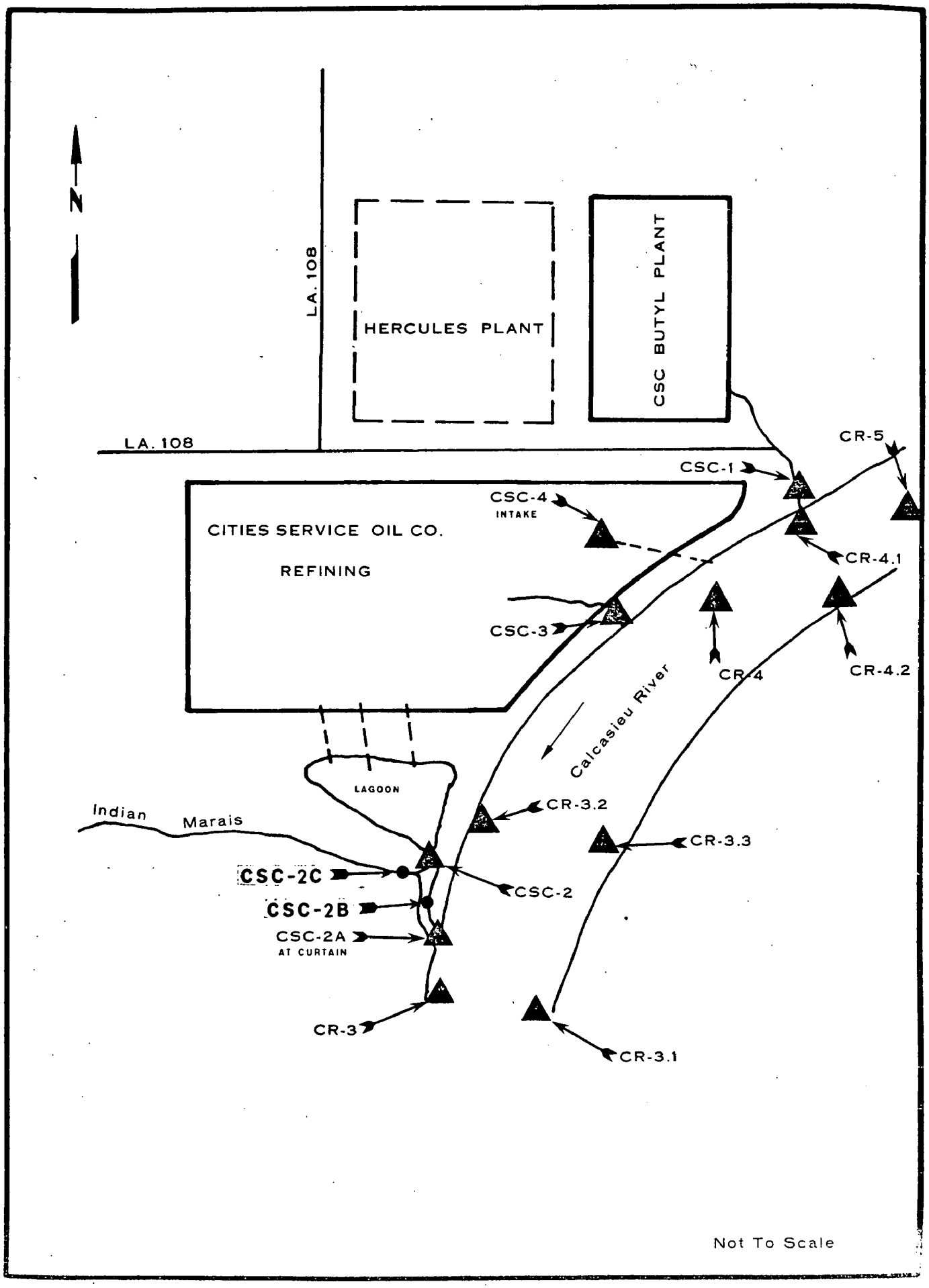

Figure 2. Effluent & Receiving Water Sampling Locations for Cities Service Oil Co. - Butyl Plant & Refinery

Control Stations, CR-1 and CR-11.2 [Table 1], are located in the Lower Calcasieu River so as to have the least possible contamination from industrial wastes. Station CR-1 is located downstream from industrial discharges and closer to the Gulf of Mexico than are all the other stations. Station CR-11.2 is located upstream of most industrial discharges and has water with lower salinity levels than has Station 1.

DATA REPORTED TO LOUISIANA STREAM CONTROL COMMISSION

The Louisiana Stream Control Commission approved (December 16, 1970) the discharge levels of certain materials based on data submitted by the Cities Service Oil Company for its Butyl plant. A summary of the information from the Commission files is as follows:

Quantity of Discharge:	0.9 cfs
Temperature:	65-87°F.
Turbidity:	25-60 JTU
True Color:	20-30
Organic Materials (oil):	17 lbs/day - 3 ppm
Inorganic Materials:	4300 lbs/day - 900 ppm
Toxic Materials:	
Chromium	0 lbs/day - 0 ppm
Zinc	4 lbs/day - 1 ppm
Mercury	0 lbs/day - 0 ppm
Dissolved Oxygen:	50% Saturation

PROPOSED WASTE TREATMENT

The Company's laboratory personnel are presently experimenting with new treatment processes; no schedule for upgrading treatment has been made known. The intent, according to Mr. Kirby, is to reuse treated wastewater as cooling make-up water in the Butyl plant.

CONCLUSIONS

1. The present discharges of heavy metals, carbonaceous materials, suspended solids, and oil and grease, constitute violations of Section 407, Rivers and Harbors Act of 1899 (33 USC: 401-413).

2. The stream near the effluent discharge is toxic to native shrimp.

3. An effort is being made to develop and implement a suitable treatment and reuse scheme, but no implementation schedule was made known to the EPA investigators.

RECOMMENDATIONS

It is recommended that:

1. The Office of Enforcement, EPA, in cooperation with appropriate State and local authorities, monitor progress toward implementation of suitable treatment processes at The Cities Service Oil Company Butyl Rubber plant.

2. If a schedule for implementation of suitable treatment is not in effect by June 1, 1972, consideration be given to initiating appropriate abatement actions against the Company for the discharge of chromium; carbonaceous materials; suspended solids; and oil and grease to the Calcasieu River, a navigable stream.

3. When a suitable schedule is implemented, the Office of Enforcement, EPA, monitor progress toward completion, and take appropriate action at any time that the Company falls behind the schedule.

4. The Corps of Engineers permit, to be issued, limit concentrations of BOD; COD; TOC; of suspended solids; oil and grease; heavy metals; and

complex organics to levels consistent with best available treatment and with the water quality standards for the Lower Calcasieu River.

BACKGROUND INFORMATION

Facility Description

The plant operates continuously. The production work force includes approximately 1000 employees.

The refinery produces propane; propylene; *o*-xylene and other aromatic chemicals; aviation gas; motor gas; jet fuel; kerosene; diesel fuel; furnace oil; carbon black feed; residual fuel; coke; and feed stocks for lubes, waxes, and petrochemicals.

Crude oils, light hydrocarbons (to butane), diethylglycol, and pyrrolidine are the raw materials used in the operation. Others, used in the process, include sodium hydroxide, calcium chloride, corrosion inhibitors, oxidation inhibitors, and tetraethyl lead.

Water Supply

Water for the refinery is obtained from the Calcasieu River for non-contact cooling (360 mgd). Seven wells, each rated at 1,000 gpm (1.44 mgd), provide process water, cooling water, and boiler feed.

Analyses of the river intake water [Table 4] indicate that it contained 0.2 µg/l mercury; 0.1 mg/l lead; 9 mg/l TOC; and 31 mg/l suspended solids on the day of sampling.

Existing Waste Treatment

Once-through cooling water from the power plant as well as oily wastes from the refinery and the Butyl rubber plant are treated in a 28-acre oxidation lagoon. It discharges to a second pond that was dredged in Indian Marais. The second pond's outlet, to the Lower Calcasieu River

TABLE 4

SUMMARY OF ANALYTICAL RESULTS AND FIELD MEASUREMENTS
FROM FIRST SAMPLING PROGRAM[a]

Sta	Flow[b] mgd	pH range	Conductivity µmhos/cm range	Conductivity µmhos/cm comp	Temp °C °C	TOC mg/l	TOC lb/day	COD[c] mg/l	COD[c] lb/day	Solids total mg/l	Solids total lb/day	Solids susp mg/l	Solids susp lb/day	Oil & Grease mg/l	Oil & Grease lb/day
CSC-2	290	7.3-8.2	14,000-18,000	13,600	32-37	15	36,300			9,220	22.3×10^6	38	92,000	5	12,100
CSC-2A	290	7.3-8.3	14,500-17,000	13,000	32-34	230	557,000	520	1.26×10^6	9,850	23.9×10^6	220	533,000		
CSC-3	58	7.0-7.9	13,000-16,000	12,800	33-36	13	6,300			8,710	4.2×10^6	27	13,000		
CSC-4	400	7.1-7.8	15,000-20,000	13,600	23-25	9	30,000			9,760	32.6×10^6	31	103,500		
CR-3		7.1-8.0		14,850	25-25	9.8, 13[d]				9,580		9			
CR-4		7.1-8.3		13,000	24-24	9.4, 12[d]				8,610		14			

TABLE 4 (continued)

SUMMARY OF ANALYTICAL RESULTS AND FIELD MEASUREMENTS
FROM FIRST SAMPLING PROGRAM

Sta	Cadmium	Chromium		Mercury		Copper		Lead		Aluminum	NH_3 as N	
	mg/l	mg/l	lb/day	µg/l	lb/day	mg/l	lb/day	mg/l	lb/day	mg/l	mg/l	lb/day
CSC-2	<0.05	0.02	48	0.2	0.4843	0.04	97	0.2[e]	485		10.1	24,500
CSC-2A	<0.05	0.14	340	1.0	2.422	0.11	266	4.0[e]	9,690			
CSC-3	<0.05	<0.01		0.3	0.1443	0.04	19	0.2[e]	95			
CSC-4	<0.05	<0.01		0.2	0.6680	<0.02		0.1[e]	335			
CR-3	<0.05	<0.02		4.6		<0.02		<0.1		<0.5		
CR-4												

a/ Analytical procedures are outlined in Appendix D.
b/ Flow data, provided by T. W. Kirby, compare with information collected from Louisiana Stream Control Commission files.
c/ COD analyses were performed when TOC values exceeded 20 mg/l.
d/ Two composites taken (morning and afternoon).
e/ No interference from calcium detected.

(Station CSC-2A), is equipped with a steel curtain that extends approximately three feet below the water surface. This curtain functions as a skimmer to prevent the discharge of floating oil and is hinged to a catwalk so that it can pivot with the direction of flow of the water. When there is barge traffic on the River, the curtain is observed to pivot with flows moving from the waterway upstream into the second pond. Flow through this system is approximately 288 mgd [Figure 2].

Condenser cooling water is discharged without treatment directly to the Lower Calcasieu River. This discharge amounts to approximately 57.6 mgd.

FIRST SAMPLING PROGRAM AND RESULTS

Aliquots (250 ml) were composited every four hours, commencing at 7:55 a.m., April 21, at four sampling stations in the refinery [Figure 2]. [Description of these stations and of the stream stations sampled is provided in Table 5.] A grab sample for oil and grease analyses was obtained at CSC-2 at 3:15 p.m., April 17. On April 21, at 11:00 a.m. another grab sample was taken, at Station CSC-2, for organic analysis. [Analytical results and field measurements recorded are listed in Table 4.]

Analysis of the upper pond effluent was carried out to determine complex organics [Table 6]. Normal aliphatic hydrocarbons identified in the effluent sample represent a portion of the oil and grease discharged by the Company refinery. High concentrations of phenolic compounds were also observed in the effluent. In these concentrations (as discharged from the refinery), the compounds are toxic to aquatic life and may have a detrimental effect on the receiving waters.

TABLE 5

DESCRIPTION OF EFFLUENT AND RECEIVING WATER SAMPLING POINTS

Station Number	Description
CSC-2	Effluent from the refinery lagoon at the outlet structure, approximately 1,000 ft from the Lower Calcasieu River.
CSC-2A	Samples collected at the point where the effluent from the refinery enters the Lower Calcasieu River.
CSC-2B	Samples collected at mid-depth at center of second pond dredged from Indian Marais.
CSC-2C	Effluent from two small ponds, which are part of the refinery's treatment, that are located on the south side of Indian Marais. Effluent enters Indian Marais just upstream of second pond.
CSC-3	Samples collected from the power plant effluent before it enters the Lower Calcasieu River (Dock C). Flow is approximately 40,000 gpm.
CSC-4	Cooling water supply to the refinery (approximately 200,000 gpm). Samples collected at the forebay of the pump house, (source Lower Calcasieu River).
CR-1	Lower Calcasieu River near Calcasieu Landing (upstream of intracoastal waterway), near channel marker 92 (Control Station).
CR-3	Lower Calcasieu River at Channel Marker 106, downstream from the main effluent of the Company refinery.
CR-3.1	Lower Calcasieu River, east shore opposite the main refinery discharge.
CR-3.2	Lower Calcasieu River, west shore at industrial discharge of the refinery.
CR-3.3	Lower Calcasieu River, east shore, and opposite Cities Service main refinery discharge.
CR-4	Lower Calcasieu River upstream of Cities Service refinery effluent and downstream from the Company Butyl rubber plant effluent.
CR-11.2	Lower Calcasieu River, south shore, south of Clooney Island just west of Lake Charles (Control Station).

TABLE 6

RESULTS OF ORGANIC ANALYSIS

Compound Identified	Concentration (mg/l)	Load lb/day
Dodecane	0.031	79
Heptadecane	0.022	53
Hexadecane	0.026	66
Nonadecane	0.013	33
2-Methylnaphthalene	0.013	33
o-Cresol	0.120	300
Octadecane	0.017	43
Pentadecane	0.030	76
Phenol	0.200	510
Tetradecane	0.039	99
Tridecane	0.042	107
Undecane	0.027	69
1-Methylnaphthalene	0.005	12

At the time sampling was being planned, the DFI-DC investigating team indicated to officials of the Company that, since the second pond had been dredged from a natural tributary (Indian Marais) and is subject to tidal action, the discharge from the first pond (CSC-2) should be considered to be the point of discharge and, therefore, the point to be sampled. These officials claimed that the second pond constitutes a segment of the treatment process, and that the flow past the curtain into the Lower Calcasieu River (CSC-2A) should be sampled. Since the dispute could not be resolved, it was finally agreed that both points would be sampled -- the dispute to be resolved after consultation with respective legal staffs.

Substantial differences in quality were found to exist between the two sampling points [Table 5]. Calculated loads discharged, during the 24-hour period, at CSC-2 included 36,300 lbs of total organic carbon (TOC); 92,000 lbs, suspended solids; 12,100 lbs, oil and grease; 48 lbs, chromium; 0.48 lbs, mercury; 97 lbs, copper; 485 lbs of lead; and 1.7×10^{12} calories of heat. Calculated loads discharged at CSC-2A, during the 24-hour sampling period, included 1,260,000 lbs of chemical oxygen demand (COD); 557,000 lbs, TOC; 533,000 lbs, suspended solids; 340 lbs, chromium; 2.42 lbs, mercury; 266 lbs, copper; and 9,690 lbs of lead.

Because the curtain caused the materials to be discharged at depths of at least six feet in the Lower Calcasieu River, oil and grease were not measured at CSC-2A; however, oil rises in widely dispersed patches well downstream from the curtain. Thus, it was not possible to obtain a representative sample with the equipment at hand.

The cause of the differences in the concentrations at the two points

is not clear. Possible causes include unknown discharge(s) to the second pond; unobserved discharges from Indian Marais; tidal action causing buildup in the lower ponds or scouring of bottom materials by flood tides passing beneath the curtain; and the elimination of interfering substances within the lower pond. The possibility of sampling error is discounted because various parts of the analyses and standards were carefully rechecked. Moreover, concentrations of TOC, suspended solids, lead, and mercury were at least five times greater at CSC-2A than at CSC-2. Also, all concentrations measured were higher to some degree at the outlet from the second pond. If analytical or sampling errors were involved, such a pattern would not have prevailed.

Based upon the contention by Company officials that Station CSC-2A is most representative of the discharge by the refinery, the net loads discharged during the 24-hour sampling period were calculated by adding loads from stations CSC-2A and CSC-3, and by subtracting the intake loads at CSC-4. (Flows used in calculating the loads were furnished by Company officials.) The loads thus calculated include 533,000 lbs of TOC; 443,000 lbs of suspended solids; 340 lbs, chromium; 1.9 lbs, mercury; 285 lbs, copper; and 9,400 lbs of lead. As indicated earlier, discharges of oil and grease were not determined at CSC-2A. The load discharged at CSC-2 during the 24-hour sampling period was 12,000 lbs. The discharges also added 12×10^{12} calories heat.

Survival studies, employing white shrimp, were conducted <u>in situ</u> at industrial sites Stations CR-3, 3.1, 3.2, 3.3, 4.1, and 4.2 and at 11.2 and 1 [Figure 2] following methods outlined in Appendix C. A 100 percent

shrimp mortality at all industrial site stations within a 24-hour exposure period, precluding taste and odor studies. Shrimp at Control Stations CR-11.2 and CR-1 [Figure 2] had 24-hour mortalities of 10 and 20 percent, respectively [Table 7].

A sediment sample, collected below the main discharge (station CR-3.2), was composed of black soft sediment having a strong petrochemical odor [Table 8]. Almost 20 percent of the sample was volatile materials. An organic sediment index (OSI) of 2.8 indicates an organic sludge undergoing decay and decomposition. The sediment also contained 5.4 µg/g of mercury.

TABLE 7

SURVIVAL STUDIES OF WHITE SHRIMP IN THE LOWER CALCASIEU RIVER, LOUISIANA

Station	96-Hour Survival Study[a/] Exposure Time	Number Alive	Number Dead	Percent Survival
CR-11.2 (Control)	Initial	10	-	100
	24-hour	9	1	90
	48-hour	8	2	80
	72-hour	8	2	80
	96-hour	5	5	50
CR-3.3	Initial	10	0	100
	24-hour	0	10	0
CR-3.2	Initial	10	0	100
	24-hour	0	10	0
CR-3.1	Initial	10	0	100
	24-hour	0	10	0
CR-3.0	Initial	10	0	100
	24-hour	0	10	0
CR-1 (Control)	Initial	10	0	100
	24-hour	8	2	80
	48-hour	8	2	80
	72-hour	8	2	80
	96-hour	5	5	50

a/ April 20-24, 1971

TABLE 8

ANALYTICAL RESULTS OF BOTTOM SEDIMENT SAMPLES

Station	Date	Time	Water Depth, Feet	Type[a] of bottom	Odor[a] of bottom	Volatiles %	Organic Carbon %
CR-1	4/22/71	1145	2.0	Soft mud	None	7.6	2.76
CR-3.2	4/22/71	1330	30.0	Black, soft sediment	Petro-chemical	19	8.88

Station	Nitrogen %	Organic Sediment Index	Sediment Type	Mercury[b] µg/g
CR-1	0.189	0.52	II	<0.2
CR-3.2	0.318	2.8	III	5.4

a/ General appearance and odor at time of collection.
b/ Results based on dry weight. Samples dried at 35°C for two days.

SECOND SAMPLING PROGRAM AND RESULTS

This section summarizes the results of the second sampling program of Cities Service Oil Company refinery.

As noted in the section titled "First Sampling Program and Results", discrepancies connotating differences in quality were perceived between two sampling points, CSC-2 and CSC-2A [Table 4]. Because of these discrepancies a second survey was conducted on October 22 and 23, 1971.

On October 21, 1971, T. P. Harrison, Enforcement Office, EPA, Region VI contacted officials of Cities Service Oil Company refinery to make arrangements for the re-sampling program. On October 22, 1971, J. L. Hatheway, L. R. Walz, and H. W. Boyle contacted Stan Gilliard of the refinery to outline and make arrangements for the second survey. Mr. Gilliard was cooperative and agreed to the re-sampling survey as well as to the addition of station CSC-2B. He also informed Mr. Hatheway that effective September 19, 1971, the refinery began discharging "sour water"* at a rate of 325 gpm to a deep well.

Aliquots (125 ml) were composited every two hours commencing at 12:15 p.m., on October 22, 1971, at six sampling stations in the refinery [Figure 2]. [Description of these stations is provided in Table 5.] At stations CSC-2A and CSC-2B the samples were collected at a point below the steel curtain and at mid-depth, respectively. The samples collected from the lower pond (CSC-2B) consisted of a composite of two grab samples.

On October 23, grab samples for oil and grease analysis were obtained

* "Sour water" is a trade term that identifies a process waste which contains high concentrations of hydrogen sulfide, ammonia, and phenols.

at stations CSC-2A and CSC-2 at 10:30 and 10:40 a.m., respectively. At the request of Cities Service Oil Company personnel, all collected samples were divided and a portion given to them; the remainder was forwarded to EPA laboratories for analysis. [Analytical results and field measurements of the second sampling program are listed in Table 9.]

During the 24-hour period, waste loads discharged from the refinery were calculated by adding loads from stations CSC-2A and CSC-3, and subtracting the intake loads at CSC-4. Flows used in calculating the loads were furnished by Company officials and compare with information in Louisiana Stream Control Commission files. The daily loads calculated include 25,000 lbs of COD; 3000 lbs, suspended solids; 16 lbs, chromium; 134 lbs, copper; 167 lbs, lead; 12,000 lbs of oil and grease, and 11 X 10^{12} calories of heat.

DATA REPORTED TO LOUISIANA STREAM CONTROL COMMISSION

The Louisiana Stream Control Commission approved (December 16, 1970) the discharge levels of certain materials based on data submitted by the Cities Service Oil Company for its refinery. A summary of the information from the Commission files is as follows:

Quantity of Discharge:	535 cfs
Temperature:	68-102°F
Turbidity:	25-60 JTU
True Color:	60
Organic Materials (Oil):	17,300 lbs/day - 6 ppm
Organic Materials (BOD):	98,400 lbs/day - 34 ppm
Inorganic Materials:*	100,000 lbs/day - 37 ppm

* Incoming River water would contain as much as 53,000,000 lbs/day of dissolved solids, to which the above would be added.

TABLE 9

SUMMARY OF ANALYTICAL RESULTS AND FIELD MEASUREMENTS FROM SECOND SAMPLING PROGRAM[a]

Station	Flow[b] mgd	Conductivity umhos/cm range	Temp °C range	TOC mg/l	COD mg/l	COD lbs/day	Solids total mg/l	Solids total lbs/day	Solids susp mg/l	Solids susp lbs/day
CSC-2	290	18,000-21,000	35-38	<5	190	459,000			50	121,000
CSC-2A	290	18,500-22,000	31-35	<5	140	339,000	14,500	35.1×10^6	40	97,000
CSC-2B	290	22,000	35	<5	120	291,000	14,700	35.6×10^6	40	97,000
CSC-2C				89	520		14,300		160	
CSC-3	58	16,000-22,000	35-39	<5	110	53,000	14,000	6.78×10^6	80	39,000
CSC-4	400	18,000-23,000	25-26	<5	110	367,000	14,300	47.7×10^6	40	133,000

TABLE 9 (continued)

SUMMARY OF ANALYTICAL RESULTS AND FIELD MEASUREMENTS
FROM SECOND SAMPLING PROGRAM

Station	Oil and Grease		Cadmium		Chromium		Copper		Lead[c]	
	mg/l	lbs/day	mg/l	lbs/day	mg/l	lbs/day	mg/l	lbs/day	mg/l	lbs/day
CSC-2	9	22,000	<0.01		0.03	73	0.10	242	0.19	459
CSC-2A	5	12,000	<0.01		0.03	73	0.16	387	0.14	338
CSC-2B			<0.01		0.03	73	0.14	339	0.08	194
CSC-2C			0.02		0.44		0.33		0.63	
CSC-3			0.02	10	0.02	10	0.10	48	0.06	29
CSC-4	<1		0.01	33	0.02	67	0.09	301	0.06	200

a/ Analytical procedures are outlined in Appendix C.
b/ Flow data, provided by T. W. Kirby, compare with information collected from Louisiana Stream Control Commission files.
c/ No interference from calcium detected.

Toxic Materials:	
Chromate	80 lbs/day - 0.03 ppm
Phenol	1,205 lbs/day - 0.45 ppm
Zinc	117 lbs/day - 0.13 ppm
Mercury	0 lbs/day - 0 ppm.

PROPOSED WASTE TREATMENT

Towers are being constructed at the Cities Service Oil Company refinery that will permit recirculation of cooling water. Operation of the cooling facilities will reduce flow through the ponds by approximately 130 mgd.

As noted earlier, EPA investigators were not permitted to sample the process wastes entering the pond system. As a result, the present treatment capability could not be determined. Since the detention time will remain short, reduction of the flow through the system by 130 mgd cannot be expected to increase materially the treatment efficiency. The proposed additional wastewater treatment consists principally of in-plant process control and primary treatment for the residual.

At the time of the first EPA investigation, sour water was included with the wastes treated in the pond system. A deep well system (4,900 ft) had been constructed and was being used for disposal of sour water at the time of the second investigation. The Cities Service Oil Company refinery has been issued a permit by the mineral division of the Louisiana Department of Conservation to operate this disposal well. The quantity and quality of the sour water produced is not known but the disposal well is rated at 800 pgm (1.15 mgd).

CONCLUSIONS

From the data obtained during the second sampling program, October 22 and 23, 1971, the discharged waste loads, as measured at stations CSC-2

and CSC-2A, are comparable. Waste loads at both these stations are very comparable to those measured at station CSC-2 during the first sampling program. The reason for the discrepancy between measured waste loads at CSC-2 and CSC-2A during the first survey is not readily apparent. Operation of the disposal well appears to have contributed to the reduction of waste loads discharged to the River.

1. The waste loads determined at stations CSC-2 and CSC-2A in the second survey confirm the waste load measurement at station CSC-2 in the first survey.

2. The refinery discharges carbonaceous materials; suspended solids; chromium; mercury; copper; lead; phenols; and heat to the Lower Calcasieu River, in violation of Section 407, Rivers and Harbors Act of 1899 (33 USC: 401-413).

3. Observations of receiving waters, the discharge of oil and grease at station CSC-2A (12,000 lbs/day), and the character of the bottom deposits in the Lower Calcasieu River in the vicinity of the refinery substantiate that oil and grease in objectionable quantities are being discharged by the refinery into the River.

4. River water near the refinery discharge is toxic to shrimp, one of the native forms of aquatic life found in the Lower Calcasieu River.

5. Cooling facilities, which will reduce flow through the pond system, are under construction. The pond system will continue to be used for treating the remaining waste streams and constitutes primary treatment even though ponding is no suitable treatment for refinery wastes.

6. Operation of the disposal well, if continued, may result in reduc-

tions in the amounts of ammonia and sulfides and other substances now discharged to the pond system. Such disposal is contrary to EPA policy guidelines and previous regulatory practice.

RECOMMENDATIONS

It is recommended that:

1. Consideration be given to initiating appropriate abatement actions against the Lake Charles Refinery of the Cities Service Oil Company for discharges of carbonaceous materials; suspended solids; chromium; mercury; copper; lead; phenols; and heat to the Calcasieu River.

2. The appropriate Federal District Court be requested to enjoin the Cities Service Oil Company from use of the disposal well because such practice is contrary to the public interest and may endanger public water supplies.

3. The Corps of Engineers permit, to be issued to this refinery, limit the discharge of BOD; COD; TOC; suspended solids; oil and grease; heavy metals; complex organics; and heat to levels consistent with best available treatment and with the water quality standards for the Lower Calcasieu River.

BACKGROUND INFORMATION

Facility Description

Ownership of this plant is divided as follows: approximately two-thirds by Cities Service Oil Company and one-third by Continental Oil Company, thus the name Cit-Con.

This lube and wax plant operates continuously. Of the 454 persons employed at the plant three are involved in water pollution control activities. Finished products are liquid paraffin wax; vacuum gas oil; wax slabs; finished neutral oil; finished light intermediate neutral oil; finished heavy oil; soft wax by-product; finished bright stock; and amorphous wax.

The primary raw material is topped crude. Rated plant capacity is 30,000 barrels per day of feed, of which 9,500 barrels are lube stock.

Water Supply

Water for use in this plant is obtained from a series of four wells, each of which is rated at 1,000 pgm (1.44 mgd). Approximately 1,000 gpm (1.44 mgd) are used for non-contact cooling and 2,000 gpm (2.88 mgd) for process water. Water is also used to slurry fine clay employed as a decoloring agent, to disposal pits.

Existing Waste Treatment

Wastewater discharges from this industry are treated in a large oxidation pond where gravity separation and skimming of oil and grease are provided. The wastewater flow is approximately 3.32 mgd, of which 0.43 mgd is cooling water. The oxidation pond has a retention time of about 70 days. Effluents from this pond and the clay pits discharge to an open channel that

subsequently enters Bayou d'Inde [Figure 3].

DISCUSSION OF SAMPLING PROGRAM AND RESULTS

Aliquots (125 ml) of the plant effluent were collected every two hours and composited over a 24-hour period commencing at 7:15 a.m. April 21. [Description of sampling stations is provided in Table 10.] The plant effluent samples were taken at a railroad bridge (CSC-6), located approximately 500 feet downstream of the oxidation pond [Figure 3]. At this sampling point the effluent from the clay slurry pits was thoroughly mixed with the pond effluent. A grab sample was collected, at 4:40 p.m. April 17, for oil and grease analysis. [Results of the effluent sampling are shown in Table 11.]

During the 24-hour period of sampling the lube and wax plant discharged 410 lbs of TOC; 60 lbs, NH_3-N; 630 lbs, suspended solids; and 190 lbs of oil and grease.

Shrimp survival studies were conducted in Bayou d'Inde at station CR-6.1 [Figure 3] and at Control Stations following methods outlined in Appendix C. Sediment samples were collected upstream of the lube and wax plant and at Station CR-6.2 [Table 12].

Survival studies with shrimp indicate that total mortality occurred within six hours [Table 13]. The lack of oxygen in the water or the toxicity from either industrial wastes or noxious gases (released from the sludge-covered bottom) was considered as cause of death. The 100 percent mortality precluded taste and odor tests. During this time span, at CR-11.2 and CR-1, shrimp mortalities were 10 and 20 percent, respectively.

TABLE 10

DESCRIPTION OF EFFLUENT AND RECEIVING WATER SAMPLING POINTS

Station Number	Description and Remarks
CSC-6	Effluent from oxidation pond of lube and wax plant, collected at railroad bridge approximately 500 feet downstream from pond.
CR-1	Lower Calcasieu River near Calcasieu Landing (above intracoastal waterway) near channel marker 92 (Control Station).
CR-6.1	Bayou d'Inde downstream from Cit-Con, and Cities Service petrochemical plant.
CR-6.2	Bayou d'Inde upstream of Cit-Con, and Cities Service petrochemical plant.
CR-11.2	Lower Calcasieu River, south shore, south of Clooney Island just west of Lake Charles (Control Station).

TABLE 11

SUMMARY OF ANALYTICAL RESULTS AND FIELD MEASUREMENTS[a/]

Sta	Flow	pH range	Conductivity µmhos/cm range	Conductivity µmhos/cm composite	Temp °C range	TOC mg/l	TOC lbs/day	Solids total mg/l	Solids total lbs/day	Solids susp mg/l	Solids susp lbs/day	NH_3 as N mg/l	NH_3 as N lbs/day
CSC-6	2.91	7.2-8.6	460-540	510	26-29	17	410	361	8,800	26	630	2.35	60

Sta	Oil & Grease mg/l	Oil & Grease lbs/day	Cadmium mg/l	Chromium mg/l	Chromium lbs/day	Mercury µg/l	Lead mg/l	Copper mg/l
CSC-6	8	190	<0.05	0.07	2	<0.1	<0.1	<0.02

a/ Analytical procedures are outlined in Appendix D.

TABLE 12

ANALYTICAL RESULTS OF BOTTOM SEDIMENT SAMPLES

Station	Date	Time	Water Depth, Feet	Type[a/] of bottom	Odor[a/] of bottom	Volatiles %	Organic Carbon %
CR-6.1	4/22/71	1350	15.0	Soft mud	H_2S	20	9.03
CR-6.2	4/22/71	1700		Black muck	Septic	19	7.41

Station	Nitrogen %	Organic Sediment Index	Sediment Type	Mercury[b/] µg/g
CR-6.1	0.375	3.4	III	2.0
CR-6.2	0.423	3.1	III	1.7

a/ General appearance and odor at time of collection.
b/ Results based on dry weight. Samples dried at 35°C for two days.

TABLE 13

SURVIVAL STUDIES OF WHITE SHRIMP IN THE LOWER CALCASIEU RIVER, LOUISIANA

Station	96-Hour Survival Study[a/] Exposure Time	Number Alive	Number Dead	Percent Survival
CR-11.2 (Control)	Initial	10	-	100
	24-hour	9	1	90
	48-hour	8	2	80
	72-hour	8	2	80
	96-hour	5	5	50
CR-6.1	Initial	10	0	100
	24-hour	0	10	0
CR-1 (Control)	Initial	10	0	100
	24-hour	8	2	80
	48-hour	8	2	80
	72-hour	8	2	80
	96-hour	5	5	50

a/ April 20-24, 1971

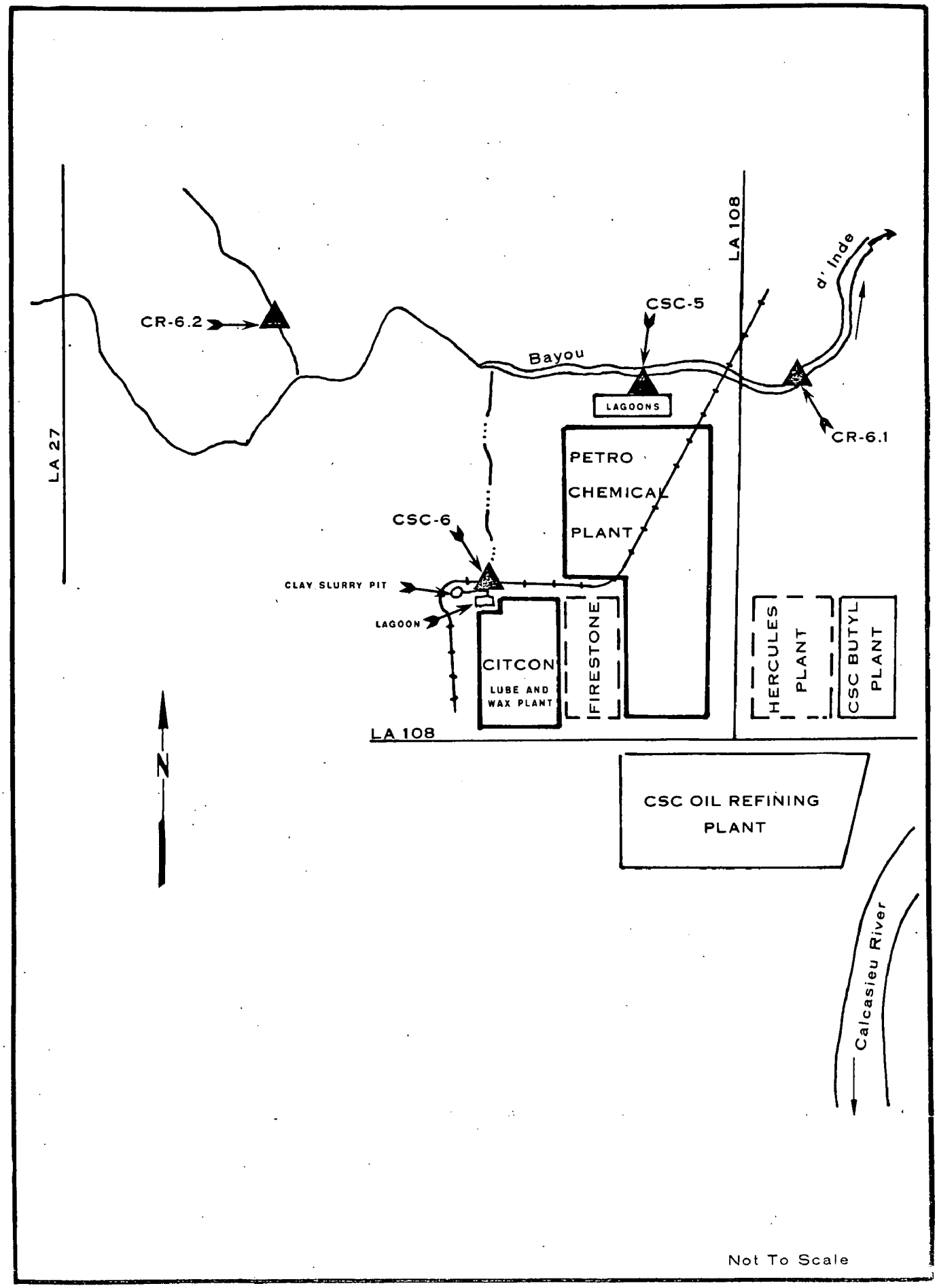

Figure 3. Effluent & Receiving Water Sampling Locations for Cities Service Oil Co. - Lube & Wax Plant (CIT-CON) & Petrochemical Plant

Sediment analyses from CR-6.1 indicated a 20 percent volatile material and an organic sediment index (OSI) of 3.4 [Table 9]. This OSI value indicates a highly organic bottom deposit that is undergoing decomposition and stabilization. Upstream of the lube and wax plant discharge the sediment was composed of decaying material, vegetation, leaves, etc. At this location the OSI was only slightly lower (3.1); likewise, the volatile material (19 percent) was lower.

DATA REPORTED TO LOUISIANA STREAM CONTROL COMMISSION

The Louisiana Stream Control Commission approved (December 16, 1970) the discharge levels of certain materials based on data submitted by the Cities Service Oil Company for its lube and wax plant. A summary of the information from the Commission files is as follows:

Quantity of Discharge:	5.1 cfs*
Temperature:	65-87°F
Turbidity:	36 JTU
True Color:	30
Organic Materials (BOD):	2870 lbs/day - 104 ppm
Phenol	825 lbs/day - 30 ppm
Organic Materials (oil):	5,520 lbs/day - 200 ppm
Toxic Materials	
Chromium	12 lbs/day - 0.42 ppm
Zinc	4 lbs/day - 0.16 ppm

* Approximately 87 percent of the 5.1 cfs is discharged to the Cities Service refinery sewers and thence to the Lower Calcasieu River; 0.7 cfs goes directly to Bayou d'Inde.

PROPOSED WASTE TREATMENT

A larger oxidation pond is being constructed for this plant. The cost for new facilities was estimated at $1.5 million. (The plant was under construction at the time of sampling.) They are scheduled to be in operation by the latter part of 1971.

CONCLUSIONS

1. The daily discharged loads of 410 pounds of carbonaceous material; 630 pounds of suspended solids; and 190 pounds of oil and grease are violations of Section 407, Rivers and Harbors Act of 1899 (33 USC: 401-413).

2. The Company is engaged in construction of new facilities for treatment of the lube and wax plant liquid wastes.

3. Results of survival tests with shrimp were inconclusive because effects of other nearby discharges could not be separated from those of the lube and wax plant.

RECOMMENDATIONS

It is recommended that:

1. The Office of Enforcement, EPA, monitor progress toward completion and operational status of the treatment facility, now under construction.

2. If suitable treatment is not operational by June 1, 1972, consideration be given to initiating appropriate abatement actions against the Company for the discharge of carbonaceous materials; nitrogenous materials; suspended solids; and oil and grease.

3. If the new treatment facilities are in operation by June 1, 1972, the discharge from the lube and wax plant be reevaluated and, if the quality does not meet applicable criteria, appropriate abatement actions be initiated.

4. The Corps of Engineers permit, to be issued, limit concentrations of BOD; COD; TOC; suspended solids; oil and grease; and complex organics, to levels consistent with best available treatment and applicable water quality standards.

BACKGROUND INFORMATION

Facility Description

The materials produced at the Cities Service Petrochemical and Ethylene-Propylene plant are propylene; ethylene; butadiene; butane and dimer; ethylene glycol; ethylene oxide; polyglycols; and ammonia.

The plant operates continuously. Of the 498 persons employed in production, three - an engineer, a chemist, and an equipment operator - are involved in water pollution control.

Rated annual capacities of the facility are 900 million lbs of ethylene; 500 million lbs, propylene; 220 million lbs, polyethylene; six million lbs, ethylene oxide; and 22 million gal. of ethylene glycol.

The raw materials employed include raw gas; ethane; by-products from the Cities Service Oil Company refinery identified only as C_2 stream and C_3 mix; propane; butadiene; nitrogen; hydroformer gas; platformer gas; caustic soda; and sulfuric acid.

Water Supply

Water is obtained from seven wells, each of which is rated at 1,000 gpm (1.44 mgd). This water is used for cooling water makeup, boiler feed, and process water. Approximately 223 mgd of cooling water is recirculated through the cooling systems. The condensate from the cooling water is sold to a neighboring industry.

Existing Waste Treatment

The wastewater discharge from this industry is approximately 3 mgd. Treatment consists of neutralization; oil separation (gravity); and three

aerated lagoons -- totalling five acres, which are operated in series. The effluent from the lagoons is discharged to Bayou d'Inde.

SAMPLING PROGRAM AND RESULTS

Aliquots (250 ml) of the treated waste were collected every four hours and composited over a 24-hour period commencing at 8:40 a.m. on April 21. A grab sample was collected for oil and grease analysis at 4:15 p.m. on April 17. A grab sample for special organic analyses was collected at 11:45 a.m. on April 21. Sampling, made of the effluent from the petrochemical plants' third lagoon, was collected at the overflow structure prior to discharge in Bayou d'Inde (CSC-5). [Its locations are shown in Figure 3. Analytical results for station CSC-5 are tabulated in Table 14.]

The organic compounds [Table 15] represent the major constituents in the effluent sample. Other compounds were observed in lesser concentrations, but were not positively identified. The results demonstrate that a wide variety of aromatic chemicals are discharged by the Company's petrochemical plant. The specific toxicity of these compounds has not been determined. However, discharge of these compounds undoubtedly has a detrimental effect on the receiving water.

Net loads discharged by the petrochemical plant during the 24-hour sampling period included 59 lbs of chromium; 20,200 lbs, COD; 5,900 lbs, TOC; 180 lbs, ammonia; 2,600 lbs, suspended solids; and 165 lbs of oil and grease.

Shrimp survival tests and sediment analyses for the stations in Bayou d'Inde are discussed under the section covering waste treatment and disposal at Cities Service Oil Company lube and wax plant.

TABLE 14

SUMMARY OF ANALYTICAL RESULTS AND FIELD MEASUREMENTS[a/]

Sta	Flow	pH range	Conductivity µmhos/cm range	Temp °C range	TOC mg/l	TOC lbs/day	COD mg/l	COD lbs/day	Solids total mg/l	Solids total lbs/day	Solids susp mg/l	Solids susp lbs/day	NH_3 as N mg/l	NH_3 as N lbs/day
CSC-5	3.95	9.2-9.7	1,000-1,600	26-28	180	5,900	612	20,200	868	28,600	78	2,600	5.35	180

Sta	Oil & Grease mg/l	Oil & Grease lbs/day	Cadmium mg/l	Chromium mg/l	Chromium lbs/day	Mercury µg/l	Mercury lbs/day	Lead mg/l	Copper mg/l	Copper lbs/day
CSC-5	5	165	<0.05	1.8	59	0.8	0.0264	<0.1	0.09	3

a/ Analytical procedures are outlined in Appendix D.

TABLE 15

RESULTS OF ORGANIC ANALYSIS

Compound Identified	Concentration (mg/l)	Load lb/day
2-Methylnaphthlene	0.030	1.1
1-Methylnaphthalene	0.025	0.9
2,6-Dimethylnaphthalene	0.015	0.5
Indan	0.007	0.3
Indene	0.026	0.9
m-Xylene	0.008	0.3
1-Methylindene	0.002	0.1
3-Methylindene	0.003	0.1
Naphthalene	0.053	1.9
o-Methylstyrene	0.001	0.05
m-Methylstyrene	0.02	0.8
p-Xylene	0.002	0.1
o-Xylene	0.006	0.2
Phenol	0.060	2.1
Styrene	0.031	1.1

DATA REPORTED TO LOUISIANA STREAM CONTROL COMMISSION

The Louisiana Stream Control Commission had, in its files, no information on the industrial waste discharge from the Cities Service Oil Company petrochemical plant.

PROPOSED WASTE TREATMENT

The Cities Service Oil Company is presently constructing a new kind of "extended aeration" facility in order to treat wastewaters from the petrochemical plant. This new facility, to cost approximately $3 million and scheduled to be placed in operation during 1972, should reduce the loads of COD, TOC, and suspended solids now being discharged to Bayou d'Inde.

CONCLUSIONS

1. Present discharges of chromium; carbonaceous materials; nitrogenous materials; suspended solids; complex organics; and oil and grease constitute violations of Section 407, Rivers and Harbors Act of 1899 (33 USC: 401-413).

2. Treatment facilities now under construction should reduce quantities of carbonaceous and nitrogenous materials discharged to the Lower Calcasieu River. The new facilities may also reduce quantities of complex organics and suspended solids discharged. No evidence exists, nor has any claim been made, to the effect that the new treatment will eliminate discharges of heavy metals and oil and grease.

RECOMMENDATIONS

It is recommended that:

1. The Office of Enforcement, EPA, monitor progress toward completion of new facilities for treatment of the liquid wastes generated by the plant, and that it further conduct follow-up monitoring of actions taken to reduce discharges of chromium and oil and grease.

2. If the new treatment facilities now under construction are not operational by June 20, 1973, consideration be given to initiating appropriate abatement actions against the Company for discharges of carbonaceous and nitrogenous materials, suspended solids, and complex organics.

3. If the new treatment facilities are on-line by June 30, 1973, the treatment provided be reevaluated, and abatement measures, as needed, be initiated.

4. The Corps of Engineers permit, to be issued this industry, limit discharges of BOD; COD; TOC; heavy metals; suspended solids; complex organics; and oil and grease to levels consistent with best available treatment and water quality standards for the Lower Calcasieu River.

REFERENCES

1/ Rivers and Harbors Act of 1899, 33 U.S.C. 401-413, Section 407 referred to as Refuse Act of 1899.

2/ Federal Water Pollution Control Act, 33 U.S.C. 466 et seq, as amended by the Federal Water Pollution Control Act Amendments of 1961-(PL 87-88), the Water Quality Act of 1965-(PL 89-234), the Clean Water Restoration Act of 1966-(PL 89-753), and the Water Quality Improvement Act of 1970-(PL 91-224).

3/ U. S. Department of Commerce, Environmental Science Service Administration Coast and Geodectic Survey, *Atlantic Coast Sixth (1967) Edition* 163-165.

APPENDIX A

APPLICABLE WATER QUALITY REGULATIONS

APPENDIX A

APPLICABLE WATER QUALITY REGULATIONS

General

The Calcasieu River is a navigable waterway in law and in fact.[1/] Large ocean-going vessels travel up the Calcasieu River to Westlake, Louisiana. The remainder of the Calcasieu River upstream of Westlake is also used for navigation. Similarly, the lower portion of the Calcasieu River complex can be classified as a coastal water in that tidal influences are felt for significant distances upstream of the point where the Calcasieu joins the Gulf of Mexico. In compliance with the Federal Water Pollution Control Act, as amended, the State of Louisiana established water quality standards for interstate streams, coastal waters, and streams discharging into coastal waters. These standards were approved by the Secretary of the Interior. The Calcasieu River is also subject to the provisions of Section 407 of the 1899 Rivers and Harbors Act (the Refuse Act), and the oil discharge regulations established pursuant to the Water Quality Improvement Act of 1970.

Water Quality Standards

The State of Louisiana divided the Calcasieu River from the Gulf of Mexico to its origin into three distinct zones for the purpose of establishing water quality standards: (1) Zone 1, the Calcasieu River from its origin to the Salt Water Barrier; (2) Zone 2, the Calcasieu River from the Salt Water Barrier to the upper end of Moss Lake; and (3) Zone 3, that portion of the Calcasieu River from the upper end of Moss Lake to the Gulf of Mexico. Louisiana State Water Quality Standards for the Calcasieu River

describe a series of present uses of that river. They are industrial supply, primarily cooling water in the Lake Charles area; propagation of aquatic life for commercial fishing, including shellfish; irrigation water for considerable acreage of river; recreational use, including water contact sports; navigational use from the Lake Charles area to the Gulf of Mexico; and finally, carriage of municipal and industrial wastes.

Conditionally, the State indicated that they expected changes in the usage of this water with the progression of time. Primarily, these changes will take the form of municipal water supply in the upper reaches, carriage of treated municipal and industrial wastes in the lower area, and increased use for industrial supply.

No water quality standards have been established for the following tributaries: Bayou d'Inde, Bayou Verdine, Contraband Bayou, English Bayou, Houston River, Mill Creek and Palmetto Creek, all intrastate waters. The Standards established for the Calcasieu River follow.

Zone 1 - The River from Its Origin to the Salt Water Barrier

General criteria were established in Zone 1 by the Louisiana State Stream Control Commission in 1968. These criteria state that no discharge to Zone 1 shall result in conditions in the stream that will adversely affect the public health or use of the water (i.e. municipal and industrial supplies, recreation, propagation of aquatic life, etc.).

Specific criteria are as follows:

pH	From 6.0 to 8.5
Dissolved Oxygen	Not less than 50 percent saturation at existing water temperature.

Temperature	Not to be raised more than 3°C above normal ambient water temperature nor to exceed an absolute maximum of 36°C.
Oil and Grease	No oil slicks of free or floating oil are present in sufficient quantities to interfere with the designated uses nor shall emulsified oils be present in the same quantity.
Toxic Materials	None present in quantities that alone or in combination will be toxic to animals or plant life, but in all cases the level shall not exceed a $TLM_{48/10}$.
No foaming or frothing materials	
Coliform Density	1600/100 ml, calculated as the most probable number, as a monthly mean. However, 10 percent of the samples may exceed the previous number up to 5420/100 ml in any one month.
Other Materials	Limits on other substances not heretofore specified shall be in accordance with recommendations set by the Louisiana Stream Control Commission and/or by the Louisiana State Board of Health for municipal raw water sources.

Zone 2 - The Calcasieu River from the Salt Water Barrier to the Upper End of Moss Lake

General criteria for this zone indicate that, at present, the water is suitable for propagation of aquatic life, recreation, navigation, and low grade industrial supply when necessary adaptations are made by industry. No discharge is to be permitted that will result in stream conditions that will adversely affect public health, propagation and harvesting of aquatic life, recreation and navigation, or impose additional burdens of adaptation on industrial use.

Specific criteria for Zone 2 are shown in the following table:

pH	6.0 to 8.5
Dissolved Oxygen	Not less than 50 percent saturation at the existing temperature.
Temperature	Not to be raised more than 3°C above normal ambient water temperature nor to exceed an absolute maximum of 36°C.
Oil and Grease	There shall be no slicks of free or floating oil present in sufficient quantities to interfere with the designated uses nor shall emulsified oils be present in the same quantity.
Toxic Materials	None present in quantities that alone or in combination will be toxic to animals or plant life, but in all cases the level shall not exceed a $TLM_{48/10}$.
No foaming or frothing materials	
Coliforms	The monthly median for coliform density shall not exceed 542/100 ml (MPN) nor shall this count exceed 1750/100 ml in more than 10 percent of the samples in any one month.

Zone 3 - The Calcasieu River from the Upper End of Moss Lake to the Gulf of Mexico

The general criteria for this zone indicate that during periods of low flow the high mineral content of the water approaches that of the marine water itself. This mineral content is caused by tidal intrusion. Therefore, no discharge shall produce conditions in the stream adversely affecting public health or the use of waters for propagation and harvesting of aquatic life, recreation, or navigation.

Specific criteria for this zone are as follows:

pH	From 6.0 to 8.5
Dissolved Oxygen	Not less than 60 percent saturation at existing water temperature.
Temperature	Not to be raised more than 3°C above normal ambient water temperature nor to exceed an absolute maximum of 36°C.
Oil and Grease	No oil slicks of free or floating oil are present in sufficient quantities to interfere with the designated uses nor shall emulsified oils be present in the same quantity.
Toxic Materials	None present in quantities that alone or in combination will be toxic to animals or plant life, but in all cases a level shall not exceed a $TLM_{48/10}$.
No foaming or frothing materials	
Coliforms	The monthly median shall not exceed 70/100 ml nor shall this count exceed 230/100 ml in more than 10 percent of the samples in any one month.

The Rivers and Harbors Act of 1899 (Refuse Act)

The Rivers and Harbors Act of 1899 prohibits the discharge of industrial wastes to navigable waters without a permit from the U. S. Army Corps of Engineers. Section 407 of the Act (referred to as the Refuse Act) makes it unlawful to discharge from any "... manufacturing establishment, or mill or any kind, any refuse matter of any kind or description whatever, other than that flowing from streets and sewers and passing therefrom in a liquid state, into any navigable water of the United States, or into any tributary of any navigable water from which the same shall float or be

washed into such navigable water ..." provided that a discharge may be permitted under certain conditions specified by the Corps of Engineers.

Executive Order No. 11574, Administration of the Refuse Act Permit Program, signed by President Nixon on December 23, 1970, tightens enforcement of the Refuse Act of 1899 by requiring that all sources of industrial wastes discharging to navigable waters or their tributaries must apply to the Corps of Engineers for permits to continue such discharges. All sources of industrial wastes investigated during this study will thus need to apply for such permits.

Water Quality Improvement Act of 1970

On September 11, 1970, Federal regulations regarding the discharge of oil to navigable waters were established pursuant to the provisions of Section 11(b)(3) of the Federal Water Pollution Control Act, as amended by the Water Quality Improvement Act of 1970. This legislation required the President to publish, in the Federal Register, rules regarding the allowable discharge of oil to navigable water from any source. Subsequently, the President published rules which specifically stated:

(1) That discharges of oil shall not occur in amounts which violate applicable water quality standards, or;

(2) That discharges of oil shall not occur in amounts to cause a film or sheen upon or discoloration of the surface of the water or adjoining shorelines or cause a sludge or emulsion to be deposited beneath the surface of the water or upon adjoining shorelines.

APPENDIX B

CUSTODY OF SAMPLES

APPENDIX

CUSTODY OF SAMPLES

Special procedures were employed during the field investigations of waste sources in the Calcasieu River Basin to insure that a chain of custody was documented for water quality samples potentially useful as evidence for enforcement actions. This documentation was designed to maintain a record of the collection and source of each sample, as well as of the personnel involved in the handling, preparation, and disposition of each.

A unique "custody" number was assigned to each of the Company's waste effluent samples collected. This number was recorded on the sample tag, the corresponding "custody" information sheet, and on the laboratory receipt log.

As each sample was collected, a labeled tag was attached to each bottle or container. The tray information recorded on the tag included the "custody" number; the sampling station number and description; the time and date of collection; the types of analyses to be performed on the sample by the laboratory; the types of preservatives added [see Appendix D Analytical Procedures]; and the personnel collecting the sample and performing the sample preservation. Sample containers were placed in plastic bags and the bags sealed with paper tape bearing the initials of the individual packaging the sample. The intact seal and bag guaranteed the integrity of the sample during shipment.

A special "custody" information sheet was prepared for each "custody" number assigned. In addition to information being recorded on the sample

tag, the information sheet recorded the laboratory to which the sample was sent, the time and method of shipment, and the carrier. Federal Government bills-of-lading provided additional records of the shipments made.

Upon arrival of each shipment at its destination, laboratory personnel recorded the time and date of receipt; the number and type of samples received; and the analyses to be performed. This documentation procedure maintained a "custody" record for the field-to-the-laboratory transit. Each analytical laboratory involved (Division of Field Investigations-Denver Center; Division of Field Investigations-Cincinnati Center; Analytical Quality Control Laboratory, Cincinnati, Ohio; and the Southeast Water Laboratory, Athens, Georgia) then maintained custody of each sample, using procedures and records standard for the specific laboratory.

This special "custody" documentation was employed for industrial waste effluent samples only. No "custody" numbers were assigned for water and sediment samples collected from streams. Normal documentation procedures including tagging of samples, as discussed above, and logging of field measurements were followed.

APPENDIX C

BIOLOGICAL STUDY METHODS FOR PALATABILITY AND SURVIVAL STUDIES

Lower Calcasieu River
Louisiana
(April 20-24, 1971)

APPENDIX C

STUDY METHODS

Common white, or lake, shrimp (*Penaeus setiferus*), sized from 90-110 mm,* were used for survival and palatability studies in the Lower Calcasieu River. Shrimp were captured by bottom seining at 5-minute intervals in Lake Calcasieu near Turner's Bay. The catch was released from the seining net into a holding tub. These test shrimp were transferred, with extreme care, employing a nylon dipnet, or by hand, from the tub to an aerated acclimation tank filled with clean water from Lake Prein. Shrimp exposure out of the water was kept to a minimum.

After a 24-hour acclimation period in the tank, less than ten percent of the shrimp were found in distress or dead because of the previous day's netting and handling. These were culled from the tank. Live, healthy shrimp were taken from the holding tank, decapitated, wrapped in foil, and frozen with dry ice for use as a taste and odor reference sample. The remaining live, healthy shrimp were used for survival and palatability tests.

At selected stations, wire, minnow baskets were attached to floats and suspended at 1-foot depths in the River. Cloth net bags, measuring 12 by 24 inches and having a mesh opening of one-quarter inch, were placed inside the baskets. Live shrimp were carefully transferred from the holding tank to cloth net bags inside the wire baskets. This basket apparatus permitted free circulation of River water through the cages, retained the test shrimp, and reduced predation by crabs.

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* Determined by measuring from the tip of the rostrum to the end of the telson.

Flavor and Odor Evaluation (Field and Laboratory Procedures)

Baskets, each containing six shrimp, were placed at control stations and near the Company's effluents in the Lower Calcasieu River and its tributaries. After a 6-hour River exposure near the Company's discharge, the shrimp were retrieved and examined. Survivors were decapitated, wrapped, in foil, and frozen with dry ice. These frozen shrimp were shipped to the Department of Food Science and Technology at Oregon State University, Corvallis, Oregon, for flavor and odor evaluations by a panel of experienced judges.

Odor Test -- At the Oregon State University facility, the wrapped, frozen shrimp were transferred from the shipping container to a -10°F freezer. Later, the shrimp were removed from the freezer and placed at 40°F. until defrosted, then cooked in eight ounces of unsalted boiling water for five minutes. The cooked shrimp were quickly peeled and then tightly wrapped with plastic film. The cooking water was poured into 100 ml beakers and the beaker then tightly covered with aluminum foil. Each respective sample of shrimp and cooking water was placed on a plate coded with a 3-digit random number.

The reference sample* was divided into four portions, two of which were placed on coded plates and the other two on plates marked "Ref." These shrimp were then alloted to two groups and placed on opposite counters for odor testing, with the first sample in each group being a "Ref" sample. Half of the judges smelled one group first and then smelled the other,

* Shrimp that were kept in aerated Lake Prien water and not exposed to River water near industrial discharges.

with a 3- to 5-minute wait between groups. The judges were asked to sniff both the shrimp and the cooking water and score the intensity of "off-odor" as related to the reference sample. Re-sniffing the reference sample was allowed. Thirty minutes after the first odor test was completed, the plates were recoded with new 3-digit random numbers, the order changed, and a second test conducted by the same ten judges.

Flavor Test -- Each shrimp was cut into four pieces and each respective sample mixed, then served in paper cups coded with 3-digit random numbers. The coded cups were randomly placed on two serving trays, each of which contained a labeled and a coded "Ref" sample. The trays were served in balanced order to the judges seated in individual testing booths lighted with yellow-orange light. The judges were asked to score the degree of "off-flavor" and the overall desirability of the samples on a 7-point scale. (0=extreme "off-flavor" and 7=no "off-flavor.") Because the sample size varied from one to six shrimp, only five judges were served on the flavor panel. Because there was only one shrimp in four of the 96-hour exposure samples, only two judges received these samples.

Survival Tests

Baskets, each containing ten shrimp, were placed at "flavor evaluation test" stations and elsewhere. These shrimp were used as test animals for 96-hour survival studies. At the termination of each 24-hour exposure period, mortalities were recorded and the surface water near each basket was tested for pH, temperature, and salinity.

Shrimp that survived the 96-hour exposure were tested for flavor in the manner described above.

APPENDIX D

ANALYTICAL PROCEDURES

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ANALYTICAL PROCEDURES

Grab, or 24-hour composite, samples of water, industrial waste, and bottom sediments were collected in the Lake Charles area by DFI-DC personnel. Samples were preserved when collected as outlined in the Federal Water Quality Administration's Manual for the Chemical Analysis of Water and Wastes.[1/]

One-liter grab samples were collected in glass containers from each Company's effluent suspected of containing oil and grease. The samples were preserved with 2 ml concentrated H_2SO_4/l and shipped on ice to the Division of Field Investigation-Denver Center. Within 24 hours after collection, the samples were tested for oil and grease, according to the procedure outlined in Standard Methods for the Examination of Water and Waste Water[2/] - *with the exception that n-hexane was used as the extraction solvent instead of petroleum ether.* Because only single grab samples were taken from each effluent, the results may not be representative of the composite daily discharge.

Twenty-four-hour composite samples were collected at each of the Company's effluents. One liter of the sample was preserved with 2 ml concentrated H_2SO_4 for total organic carbon (TOC), chemical oxygen demand (COD), ammonia nitrogen (NH_3-N), and organic nitrogen (org.-N) analyses. One liter was preserved with 5 ml concentrated HNO_3 for metals analyses and one liter was left untreated for total and suspended solids analyses.

Water and effluent samples specified for metals analyses were shipped,

air-freight, to the Division of Field Investigations-Cincinnati Center. These samples were analyzed for cadmium (Cd), copper (Cu), Lead (Pb), chromium (Cr), zinc (Zn), aluminum (Al), and nickel (Ni) by atomic absorption spectrophotometry. All samples were analyzed for total mercury (Hg) according to the flameless AA procedure of Hatch and Ott.[3/]

Other samples were shipped, air-freight, to the Analytical Quality Control (AQC) Laboratory in Cincinnati where they were analyzed, by DFI-DC personnel, according to procedures described in the FWQA Manual.[1/]

These samples were tested for TOC by injection of homogenized 100 µl aliquots into a Beckman Model 915 Carbon Analyzer after having been purged with nitrogen gas for five to ten minutes. Injections were made in duplicate and triplicate; the average peak height was taken for comparison to a standard curve. In general, reproducibility was within five percent. Industrial waste samples with more than 20 mg/l TOC were also analyzed for COD. These determinations were made according to the procedure for "high level COD", (i.e., digestion with 0.25N $K_2Cr_2O_7$). For this analysis sufficient mercuric sulfate was added to each sample to tie up the chloride ions -- as determined by titration with mercuric nitrate. In general, each sample was tested only once, although one duplicate analysis was reproducible within eight percent. Both NH_3-N and org.-N were determined using the micro-Kjeldahl apparatus. Consequently, all reagent concentrations were scaled down to one-tenth of the level of the regular Kjeldahl procedure. Several duplicate analyses were performed with reproducibilities of four and six percent.

Total and suspended solids were determined on the unpreserved samples.

The residues were dried at 105°C.

Bottom sediment samples were collected with an Eckman Grab Sampler at selected sites along the Calcasieu River and in the vicinity of waste discharges. The muds were packed in Whirlpack bags, frozen, and shipped air-freight to the AQC Laboratory in Cincinnati.

Samples, when thawed, were air-dried at 35°C for two days under a stream of clean, dry air. The percent volatiles were calculated from the weight loss after heating the dried sample at 600°C for one hour. The percent carbon and organic nitrogen were determined by the procedures outlined by Ballinger and McKee.[4/] The organic sediment index (OSI) was calculated as the product of the percent carbon and percent organic nitrogen.

Mercury in the dried sediments was determined by an adaptation of the "wet digestion/flameless AA procedure" for mercury in fish developed by Uthe, et al.[5/] Standard additions using mercuric chloride or methyl mercuric chloride were made on each sample; recoveries ranged from 87 to 122 percent throughout the 20 samples.

One-liter grab samples were collected from the Company's effluents for organic characterization. Immediately after collection, the samples were frozen and shipped, air mail-special delivery, to the Southeast Water Laboratory, Athens, Georgia. The samples were thawed, then extracted with chloroform. Chloroform extracts were concentrated to one ml or less and injected into a Perkin Elmer Model 900 gas chromatograph. Conditions were adjusted to obtain the best resolved chromatogram by using open tabular columns of Carbowax 20 M or SE-30. Once the conditions were selected, the

column effluent was directed into a Perkin Elmer-Hitachi Mass Spectrometer, Model RMU-7. Mass scans were made of all major peaks. Identity of the extract components was confirmed by injecting known compounds under the same conditions and comparing both the retention time and the mass spectrum.

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